

Topological quantum phase transition driven by anisotropic spin-orbit coupling in trinuclear organometallic coordination crystals

J. Merino

*Departamento de Física Teórica de la Materia Condensada,
Condensed Matter Physics Center (IFIMAC) and Instituto Nicolás Cabrera,
Universidad Autónoma de Madrid, Madrid 28049, Spain*

A. C. Jacko, A. L. Khosla, and B. J. Powell

School of Mathematics and Physics, The University of Queensland, Brisbane, Queensland 4072, Australia
(Dated: June 27, 2016)

We show how quasi-one-dimensional correlated insulating states arise at two-thirds filling in organometallic multinuclear coordination complexes described by layered decorated honeycomb lattices. The interplay of spin-orbit coupling and electronic correlations leads to pseudospin-1 moments arranged in weakly coupled chains with highly anisotropic exchange and a large trigonal splitting. This leads to a quantum phase transition from a Haldane phase to a topologically trivial phase as the relative strength of the spin-orbit coupling increases.

PACS numbers: 71.30.+h; 71.27.+a; 71.10.Fd, 75.10.Kt

Introduction. In recent years there has been intense research activity on the effect of spin orbit coupling (SOC) in the electronic structure of weakly interacting materials since the discovery of topological band insulators [1, 2] (TBI). TBI are predicted to occur in certain solids with electron-like quasiparticles in the presence of strong SOC as is found in compounds containing the heavy elements such as: Bi, Pb, Sb, Hg and Te. In materials with partially filled localized orbitals, renormalization effects induced by strong Coulomb repulsion effectively enhance the SOC leading, for instance, to topological Mott [3, 4] or Kondo [5] insulators. In Ir-based compounds such as Na_2IrO_3 and Li_2IrO_3 the emergent $J = 1/2$ pseudospins arranged in a honeycomb lattice interact through anisotropic spin exchange couplings of the Kitaev-Heisenberg type [6–9]. Kitaev’s honeycomb model can be solved exactly [10] sustaining a topological quantum spin liquid state with Majorana fermion excitations which may have been recently observed in the Kitaev candidate material [11] $\alpha\text{-RuCl}_3$. This illustrates how novel quantum phases of matter arise from the interplay of strong Coulomb repulsion and SOC in certain materials.

Molecular materials are ideal playgrounds to explore strong electronic correlation effects in low dimensions [12, 13]. Although SOC effects are generally weak in organic systems [14], organometallic complexes provide a route for enhancing SOC [15]. Llusar *et al.* have synthesized a particularly interesting family of trinuclear organometallic coordination complexes [16, 17] with ligands that facilitate electronic transport between molecules including $\text{Mo}_3\text{S}_7(\text{dmit})_3$, $\text{Mo}_3\text{Se}_7(\text{dmit})_3$, $\text{Mo}_3\text{S}_7(\text{dsit})_3$, and $\text{Mo}_3\text{Se}_7(\text{dsit})_3$ (dmit= S_5C_3 , dsit= $\text{Se}_2\text{S}_3\text{C}_3$). For example, the low-energy electronic structure of $\text{Mo}_3\text{S}_7(\text{dmit})_3$ crystals [18] is described by three Wannier orbitals per molecule that are hybrids of the Mo d -orbitals and the

dmit molecular orbitals leading to narrow band structures with appreciable SOC [19, 20]. The Mo atoms, and hence the Wannier orbitals, form a layered structure with a decorated honeycomb lattice in the basal plane [19], as shown in Fig. 1. In the c -direction, the triangular $\text{Mo}_3\text{S}_7(\text{dmit})_3$ complexes arrange in tubes reminiscent of the CrAs tubes formed in the recently discovered superconductor $\text{K}_2\text{Cr}_3\text{As}_3$ [21, 22].

At two-thirds filling in the presence of strong Coulomb repulsion and no SOC, a correlated insulator consisting of spin-1 effective moments coupled through an isotropic antiferromagnetic interaction arises [23–25]. In this Letter, we derive the effective superexchange model for trinuclear crystals including SOC. SOC entangles the spin and orbital degrees of freedom leading to pseudospin-1 moments, \mathbf{S}_m , which interact via anisotropic exchange interactions. The SOC also introduces a trigonal splitting of the triplet into a lower energy $\mathcal{S}_m^z = 0$ state and a $\mathcal{S}_m^z = \pm 1$ doubly degenerate state. Surprisingly, we also find that the effective dimensionality of the pseudospin model is strongly affected by the strength of the electronic correlations: with increasing Hubbard U the pseudospin-1 model becomes increasingly one-dimensional, even though the original crystal is almost isotropic. At large trigonal splitting, a ‘ D -phase’ consisting of the tensor product of $\mathcal{S}_m^z = 0$ states on each complex, occurs. Thus, our analysis suggests that a topological quantum phase transition from a Haldane phase to a topologically trivial D -phase can be induced by increasing the SOC.

Pseudospin-1 moments in trinuclear complexes. We first analyze the local effective spin degrees of freedom arising at each isolated trimer due to the combined effect of Coulomb repulsion and SOC. We construct our model based on the Wannier orbitals found in recent density functional calculations [19, 20] and we model each com-

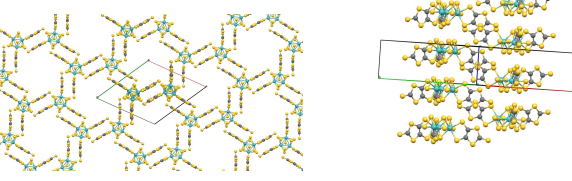


FIG. 1: (Color online) Crystal structure of $\text{Mo}_3\text{S}_7(\text{dmit})_3$. a) In the a - b plane the triangular molecules form a honeycomb lattice. As each complex contains three Wannier orbitals this results in a decorated lattice, which extrapolates between the Kagome and graphene lattices [19]. b) A complexes stack in chains along the c -axis resulting in a triangular tube arrangement of the Wannier orbitals.

plex via a Hubbard-Heisenberg model on a triangle with one orbital per site. In molecules with cyclic symmetry, such as the C_3 symmetry of a $\text{Mo}_3\text{S}_7(\text{dmit})_3$ complex, the leading SOC term in the effective low-energy Hamiltonian couples the electron spin to currents running around the complex [20], which carry a ‘molecular’ angular momentum, \mathbf{L}_m . For molecules with N -fold rotation axes the angular momentum carried by this current is $l = (N-1)/2$ if N is odd [20]; for a $\text{Mo}_3\text{S}_7(\text{dmit})_3$ complex $N = 3$ and $l = 1$. Thus the Hamiltonian for the m th complex is $H_c = H_0 + H_{\text{int}} + H_{\text{SO}}$, where

$$\begin{aligned} H_0 &= -t_c \sum_{\langle ij \rangle \sigma} \left(c_{mi\sigma}^\dagger c_{mj\sigma} + H.c. \right) \\ H_{\text{int}} &= U \sum_i n_{mi\uparrow} n_{mi\downarrow} + J_F \sum_{\langle ij \rangle} \left(\mathbf{S}_{mi} \cdot \mathbf{S}_{mj} - \frac{n_{mi} n_{mj}}{4} \right) \\ H_{\text{SO}} &= \lambda_{xy} (L_m^x S_m^x + L_m^y S_m^y) + \lambda_z L_m^z S_m^z, \end{aligned} \quad (1)$$

$c_{mi\sigma}^{(\dagger)}$ annihilates (creates) an electron with spin σ in the i th Wannier orbital of the m th molecule, $\mathbf{S}_{mi} = \sum_{\sigma\sigma'} c_{mi\sigma}^\dagger \boldsymbol{\tau}_{\sigma\sigma'} c_{mi\sigma'}$, $\boldsymbol{\tau}$ is the vector of Pauli matrices, $\mathbf{S}_m = \sum_i \mathbf{S}_{mi}$, $n_{mi\sigma} = c_{mi\sigma}^\dagger c_{mi\sigma}$, $n_{mi} = \sum_\sigma n_{mi\sigma}$, t_c is the intramolecular hopping amplitude, U is the on-site Coulomb repulsion, and $J_F < 0$ is the direct intramolecular ferromagnetic exchange [26]. We take the z -direction along the c -direction of the crystal. We consider the three-site cluster with four electrons, relevant to $\text{Mo}_3\text{S}_7(\text{dmit})_3$ and its selenated analogs.

The single electron terms are more conveniently expressed in terms of ‘Bloch’ operators on the trimer, $b_{mk\sigma}^\dagger = \sum_j c_{mj\sigma}^\dagger e^{i\phi kj} / \sqrt{3}$, where $\phi = 2\pi/3$ and $k = 0, \pm 1$ is the eigenvalue of L_m^z [15, 20, 27]. Whence,

$$\begin{aligned} H_0 &= -2t_c \sum_{k\sigma} \cos(k\phi) b_{mk\sigma}^\dagger b_{mk\sigma} \\ H_{\text{SO}} &= \frac{\lambda_{xy}}{\sqrt{2}} (b_{m0\downarrow}^\dagger b_{m-1\uparrow} - b_{m1\downarrow}^\dagger b_{m0\uparrow} - b_{m0\uparrow}^\dagger b_{m1\downarrow} \\ &\quad + b_{m-1\uparrow}^\dagger b_{m0\downarrow}) + \frac{\lambda_z}{2} (b_{m1\uparrow}^\dagger b_{m1\uparrow} - b_{m1\downarrow}^\dagger b_{m1\downarrow} \\ &\quad - b_{m-1\uparrow}^\dagger b_{m-1\uparrow} + b_{m-1\downarrow}^\dagger b_{m-1\downarrow}). \end{aligned} \quad (2)$$

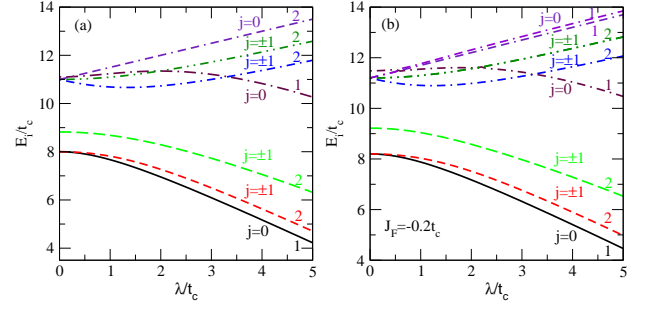


FIG. 2: (Color online) Effective pseudospin-1 moments arising in isolated trimers in the presence of SOC. The lowest-lying eigenstates of the Hubbard-Heisenberg model describing trinuclear complexes with four electrons are shown for the pure Hubbard model ($U = 10t_c$, $J_F = 0$) (a) and for non-zero intracenter exchange (b) ($U = 10t_c$, $J_F = -0.2t_c$). Only the z -component of the total angular momentum, j , is conserved labels. The degeneracies of the eigenstates are labelled by the numbers on the right-hand side of the figure. As SOC, $\lambda = \lambda_{xy} = \lambda_z$, increases the triplet state is split into a $j = 0$ state and a doubly degenerate $j = \pm 1$ state. This is described by a pseudospin-1 in the presence of a trigonal field generated by SOC.

Note that the trigonal symmetry of the complex implies that the SOC in the plane of the molecule, λ_{xy} , need not equal that in the z -direction [20]. Nevertheless, in some of the numerical work below it is convenient to set $\lambda = \lambda_{xy} = \lambda_z$ to reduce the parameter space. Spin-orbit coupling can only mix configurations with the same z -component of the total orbital momentum of the cluster: j , which is conserved (modulo 3) for any values of λ_{xy}, λ_z . With no SOC and $t_c > 0$ the low lying states are the triplet states [28]. In Fig. 2 we show how the cluster spectrum for $\lambda \neq 0$, consists on a $|j = 0\rangle$ ground state and doubly degenerate, $|\pm j\rangle$ states, expected from the combination of time reversal and trigonal (C_3) symmetries. At large U the three lowest states behave as a localized pseudospin-1. In terms of the pseudospins the effective low energy Hamiltonian for a single complex is thus $H_c^{\text{eff}} = D(\mathbf{S}_m^z)^2$; D is the trigonal splitting which increases with λ , cf. Figs. 2, 3.

Exchange interaction between neighboring trinuclear complexes. We now consider the interaction between two neighboring trimers arranged as in the $\text{Mo}_3\text{S}_7(\text{dmit})_3$ crystal. We analyze the two nearest-neighbor arrangements realized in the crystal. (A) Nearest neighbors in the a - b plane (Fig. 1(a)): a single hopping amplitude, t , connects the two molecules: $H_{\text{kin}} = -t \sum_\sigma (c_{l1\sigma}^\dagger c_{m1\sigma} + c_{m1\sigma}^\dagger c_{l1\sigma})$ [cf. inset Fig. 3(a)]. (B) Nearest neighbors in the c -direction (Fig. 1(b)) there are three hoppings, t_z , connecting equivalent orbitals i of the two molecules: $H_{\text{kin}} = -t_z \sum_{i\sigma} (c_{li\sigma}^\dagger c_{mi\sigma} + c_{mi\sigma}^\dagger c_{li\sigma})$ [cf. inset Fig. 3(d)]. In $\text{Mo}_3\text{S}_7(\text{dmit})_3$ first principles calculations find that the intramolecular hopping is nearly

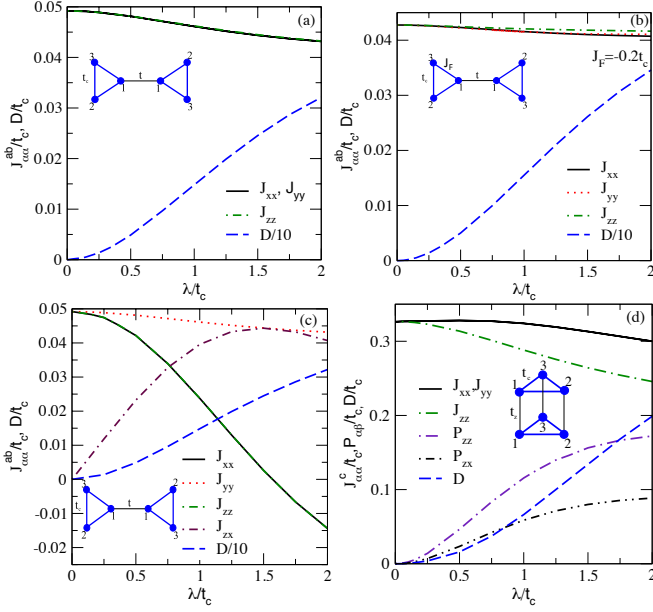


FIG. 3: (Color online) Anisotropic pseudospin exchange coupling, $J_{\alpha\beta}$, and trigonal splitting, D , induced by spin-orbit coupling in trinuclear complexes. We consider the effective interaction between the pseudospins-1 formed in two neighboring clusters in the a - b plane (panels (a)-(c)) and in the c -direction of the crystal (panel (d)). In cases (a) and (b) the two molecules are related by inversion symmetry whereas in (c) they are related by $C_2^{(z)}$ symmetry. In (d) the two molecules are related by translational symmetry. We take $U = 10t_c$ and the intracluster Heisenberg exchange $J_F = 0$ (Hubbard model) except in case (b) for which, $J_F = -0.2t_c$. Anisotropic pseudospin exchange interactions arise when inversion symmetry is broken [cases (c) and (d)] and in the presence of inversion symmetry when $J_F \neq 0$ [case (b)].

isotropic: $t_z/t = 0.87$.

We have calculated the effective exchange coupling between two neighboring clusters via two independent methods: (1) analytically via a canonical transformation to first order in $1/U$ and second order in H_{SO} and H_{kin} ; and (2) numerically with H_c treated exactly and straightforward second order perturbation theory in H_{kin} : $H_{\text{eff}}^{(2)} = \sum_{|m^0\rangle} \frac{H_{kin}|m^0\rangle\langle m^0|H_{kin}}{2E_0(4) - \langle m^0|H_0 + H_U + H_{SOC}|m^0\rangle}$, where $E_0(4)$ is the ground state energy of an isolated cluster with $N = 4$ electrons. Note that we neglect the trigonal splitting (D) in the denominator of the numerical perturbation theory. However, comparison with the canonical transformation and the eigenvalues found from exact diagonalisation shows that this approximation is extremely accurate.

(A) *Nearest neighbors in the a - b plane.* Two neighboring molecules, l and m , related by inversion symmetry satisfy: $\lambda_{m,xy} = \lambda_{l,xy}$ and $\lambda_{m,z} = \lambda_{l,z}$. The canonical transformation yields an effective pseudospin model con-

sisting of onsite and nearest neighbour terms [29]:

$$H_{ab}^{\text{eff}} = \sum_{\langle lm \rangle \alpha \beta} J_{\alpha\beta}^{ab} \mathcal{S}_l^\alpha \mathcal{S}_m^\alpha + \sum_l \left\{ D(\mathcal{S}_l^z)^2 + [K_{\pm\pm} \mathcal{S}_l^+ \mathcal{S}_l^+ + \eta K_{zz} \mathcal{S}_l^z \mathcal{S}_l^z + H.c.] \right\}, \quad (3)$$

with $\eta = 1$, $J_{\alpha\beta} = J_{\beta\alpha}$, $\alpha, \beta = x, y, z$ and angled brackets imply that the sum is over nearest neighbors only avoiding double counting. The matrix elements calculated from the numerical perturbation theory are in excellent agreement with this model, even for $\lambda > t_c$. This is not entirely surprising because λ/U remains small in this limit. The small residual terms [30] have the symmetry one would expect on extrapolating Eq. (3) to higher orders in H_{SO} .

In the pure Hubbard model ($J_F = 0$) we find numerically that there are no additional terms at higher order in $1/U$ or λ , furthermore the exchange coupling tensor is diagonal, $J_{\alpha\beta}^{ab} = J_{\alpha\alpha}^{ab} \delta_{\alpha\beta}$, and $K_{z\pm} = K_{\pm\pm} = 0$. We plot the dependence of D and $J_{\alpha\alpha}^{ab}$ on λ for fixed $U = 10t_c$ in Fig. 3(a). The exchange couplings only display a very weak anisotropy, $J_{xx}^{ab} = J_{yy}^{ab} \approx J_{zz}^{ab}$, indicating that the coupling can be described through a standard isotropic Heisenberg model in the presence of a trigonal splitting induced by SOC. Note the trigonal splitting, D , increases with increasing λ , and around $\lambda \approx 0.5t_c$, it becomes comparable to the exchange: $D \approx J_{\alpha\alpha}^{ab}$. At large values of $D \gtrsim J_{\alpha\alpha}^{ab}$, a large- D phase simply given by the tensor product of $j = 0$ states located on each cluster is expected. For instance, in the one-dimensional $S = 1$ chain a quantum phase transition from the Haldane phase to the large- D phase occurs [31–34] for $D/J \sim 0.96 - 0.971$.

Interestingly, for $J_F \neq 0$ all three diagonal exchange couplings of the tensor become different: $J_{zz}^{ab} > J_{yy}^{ab} > J_{xx}^{ab}$ (Fig. 3(b)). Hence, for $J_F \neq 0$ magnetic anisotropies between the pseudospins arise in the presence of inversion symmetry. The two molecule problem has C_{2h} symmetry once SOC is included. Since all irreducible representations of C_{2h} are one-dimensional we should then expect anisotropic couplings between the complexes that lift completely the energy level degeneracies present in the isolated trimers (Fig. 2). However, these level degeneracies persist in the spectrum of a pair of molecules for $J_F = 0$ since the in-plane exchanges ($J_{xx}^{ab} = J_{yy}^{ab}$) are equal in this case. Thus, lowering the symmetry of the Coulomb interaction (*e.g.* $J_F \neq 0$) can significantly increase the exchange anisotropy, as in models of transition metal oxides [7, 35].

Finally we mention that the trigonal splitting, D , is only weakly affected by J_F (compare Figs. 3(a) and (b)). The off-diagonal exchange, $J_{\alpha\beta}$, and non-pseudospin-conserving $K_{\alpha\beta}$ terms are non-zero, but remain small ($\sim 10^{-4}t_c$), for the parameters explored in Fig. 3(b).

It is important to understand what happens in the absence of an inversion center relating neighboring complexes. A particularly interesting case is if the two

molecules are related by a rotation of π about a z -axis bisecting the two molecules ($C_2^{(z)}$ symmetric). In the absence of SOC the $C_2^{(z)}$ symmetric and inversion symmetric models are identical. But the pseudovectorial nature of angular momenta implies that for a pair of molecules, l and m , related by $C_2^{(z)}$ symmetry $\lambda_{m,xy} = -\lambda_{l,xy}$ and $\lambda_{m,z} = \lambda_{l,z}$. With these relations the canonical transformation again yields an effective pseudospin Hamiltonian given by Eq. (3) [29]; but in contrast to the inversion symmetric case we now have $\eta = (-1)^{l+1}$ and $J_{\beta\alpha}^{ab} = -J_{\alpha\beta}^{ab}$ for $\alpha \neq \beta$. Furthermore $J_{xx}^{ab} = J_{zz}^{ab} \neq J_{yy}^{ab}$ and $J_{xy}^{ab} = J_{yz}^{ab} = 0$. The latter equality is straightforward since the hamiltonian is real when written in the orbital basis. Because the off-diagonal exchange is antisymmetric these terms are equivalent to a Dzyaloshinskii-Moriya interaction, $\mathbf{D}_{lm} \cdot \mathbf{S}_l \times \mathbf{S}_m$, [36, 37] with $D_{lm}^y = J_{zx}^{ab}/\sqrt{2}$ and $D_{lm}^x = D_{lm}^z = 0$.

Anisotropies are large in the $C_2^{(z)}$ model [Fig. 3(c)], with J_{zz}^{ab} even becoming ferromagnetic for sufficiently large SOC: $\lambda > 1.7t_c$. J_{zx}^{ab} can become as large as the diagonal $J_{\alpha\alpha}^{ab}$ exchange couplings. The non-pseudospin-conserving terms induced by SOC at $O(\lambda^2)$ are found to be small compared to the other contributions [$K_{\alpha\beta}/t_c \sim 10^{-4} - 10^{-3}$ for the parameters explored in Fig. 3(c)]. The trigonal splitting is again large, with $D \approx J_{yy}^{ab} > J_{\alpha\alpha}^{ab}$, (with $\alpha = x, z$) at moderate values of $\lambda \approx 0.45t_c$.

(B) *Nearest neighbors in the c -direction* display a tube arrangement [Figs. 1 and 3(d) inset] with the two clusters are related by translational symmetry (no inversion symmetry center). The canonical transformation yields the effective pseudospin model:

$$H_c^{\text{eff}} = D \sum_l (\mathcal{S}_l^z)^2 + \sum_{\langle lm \rangle \alpha \beta} J_{\alpha\beta}^c \mathcal{S}_l^\alpha \mathcal{S}_m^\beta + \sum_{\langle lm \rangle \alpha \beta} P_{\alpha\beta} \mathcal{S}_l^\alpha \mathcal{S}_l^\beta \mathcal{S}_m^\alpha \mathcal{S}_m^\beta, \quad (4)$$

where anisotropic biquadratic couplings, $P_{\alpha\beta} = P_{\beta\alpha}$, obey $P_{zz} = 2P_{zx} = 2P_{zy}$ and $P_{xx} = P_{yy} = P_{xy} = 0$, these relations are also confirmed numerically. The dependence of the non-zero couplings on λ is shown in Fig. 3(d). For $J_F = 0$ the off-diagonal couplings $J_{\alpha\beta}^c = 0$ for $\alpha \neq \beta$, whereas the diagonal terms behave as $J_{xx}^c = J_{yy}^c > J_{zz}^c$. Note that the isotropic version of model (4), i.e., $J_{\alpha\beta}^c = J^c \delta_{\alpha\beta}$, $P_{\alpha\beta} = P \delta_{\alpha\beta}$ and $D = 0$ is just the bilinear-biquadratic model: $H = J^c \mathbf{S}_l \cdot \mathbf{S}_m + P (\mathbf{S}_l \cdot \mathbf{S}_m)^2$, which becomes the Affleck-Kennedy-Lieb-Tasaki (AKLT) model for $P/J^c = 1/3$, which has the valence bond solid ground state which is in the Haldane phase [38].

The in-plane isotropy of the interlayer exchange ($J_{xx} = J_{yy}$, etc.) arises from the trigonal symmetry of the molecular packing (tube). In contrast to the symmetry of the in-plane packing (dumbbell) motif which allows $J_{xx} \neq J_{yy}$.

Quasi-one-dimensional pseudospin-1 model for trinuclear

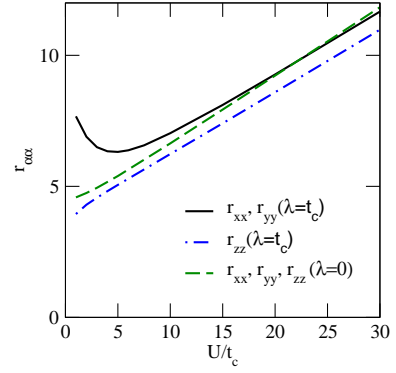


FIG. 4: (Color online) Effective one-dimensionality arising from electron correlations in trinuclear complexes. As the on-site Coulomb repulsion (U) increases spatial anisotropy of the exchange coupling, $r_{\alpha\alpha} = J_{\alpha\alpha}^c/J_{\alpha\alpha}^{ab}$, is enhanced driving the crystal to a quasi-one-dimensional system.

clear complexes. Comparing the magnitude of the diagonal exchange couplings in the a - b plane, $J_{\alpha\alpha}^{ab}$ [Fig. 3(a)-(c)], with the pseudospin exchange couplings in the c -direction, $J_{\alpha\alpha}^c$ [Fig. 3(d)], one finds significant spatial anisotropy: $r_{\alpha\alpha} = J_{\alpha\alpha}^c/J_{\alpha\alpha}^{ab} \gg 1$. Furthermore, $r_{\alpha\alpha}$ increases rapidly with U , see Fig. 4. Indeed $J_{\alpha\alpha}^{ab} \rightarrow 0$ for all α as $U \rightarrow \infty$ independent of the other parameters in the Hamiltonian [29]. In contrast all $J_{\alpha\alpha}^c$ remain finite as $U \rightarrow \infty$ in the absence of fine tuning of λ_{xy} , λ_z and t_c [29]. Thus even though the underlying electronic structure is highly isotropic ($t_z/t = 0.87$ [19]) strong electronic correlations result in a quasi-one-dimensional spin model. This emergent quasi-one-dimensionality is a consequence of the fact that nearest neighboring complexes are connected by three hopping integrals to the molecule along the c -direction of the crystal but only one hopping integral connects neighbor molecules in the ab -planes. Interference effects [39] among the possible $O(t^2)$ paths contributing to the exchange couplings make the ratio, $r_{\alpha\alpha}$, a non-universal number that increases with U [29]. Hence, in the strong coupling limit, the effective model for trinuclear complexes consists on weakly coupled antiferromagnetic pseudospin-1 chains described by model (4).

Conclusions and outlook. Our work shows how antiferromagnetic pseudospin-1 chains arise along the c -direction in crystals of trinuclear complexes such as $\text{Mo}_3\text{S}_7(\text{dmit})_3$ and its selenated analogs. With no SOC, these chains can be modeled through an isotropic $S = 1$ Heisenberg model whose ground state is in the Haldane phase [23, 25]. An important question is whether the Haldane phase is stable to the weak exchange coupling between neighbor chains arranged in the hexagonal geometry. Previous numerical work [40] has shown how the Haldane phase is unstable to the interchain exchange coupling when $r = J^c/J^{ab} > 3$ in the hexagonal geometry of $\text{Mo}_3\text{S}_7(\text{dmit})_3$ crystals. Since, $r_{\alpha\alpha} \gtrsim 5$ for all α ,

for even moderate U , we expect the Haldane phase to be the ground state of the crystal for weak SOC.

Turning on SOC introduces a trigonal splitting, D , as well as anisotropic spin exchange couplings. Thus, increasing SOC can drive the crystal from a topological Haldane phase to a trivial ‘ D -phase’ consisting of the tensor product of $j = 0$ states on each molecule. Hence, a quantum phase transition [41] may be induced in the family of materials based on $\text{Mo}_3\text{S}_7(\text{dmit})_3$ crystals by substituting, say, $\text{Mo} \rightarrow \text{W}$ [20] or $\text{S} \rightarrow \text{Se}$ [14], which effectively increases the SOC. Intriguingly, although several selenated analogs of $\text{Mo}_3\text{S}_7(\text{dmit})_3$ have been synthesized [17], little is known about their magnetic properties.

Acknowledgements. J.M. acknowledges financial support from: (MAT2012-37263-C02-01, MAT2015-66128-R) MINECO/FEDER, UE. Work at the University of Queensland was supported by the Australian Research Council (FT130100161, DP130100757 and DP160100060).

-
- [1] M. Z. Hasan and C. L. Kane, *Rev. Mod. Phys.* **82**, 3045 (2010).
 - [2] X.-L. Qi and S.-C. Zhang, *Rev. Mod. Phys.* **83**, 1057 (2011).
 - [3] D. Pesin and L. Balents, *Nat. Phys.* **6**, 376 (2010).
 - [4] W. Witczak-Krempa, G. Chen, Y. Baek Kim, L. Balents, *Ann. Rev. Cond. Mat. Phys.*, **5**, 57 (2014).
 - [5] M. Dzero, K. Sun, V. Galitski and P. Coleman, *Phys. Rev. Lett.* **104**, 106408 (2010).
 - [6] G. Jackeli and G. Khaliullin, *Phys. Rev. Lett.* **102**, 017205 (2009).
 - [7] N. B. Perkins, Y. Sizyuk, and P. Wölfle, *Phys. Rev. B* **89**, 035143 (2014).
 - [8] Y. Sizyuk, C. Price, P. Wölfle, and N. B. Perkins, *Phys. Rev. B* **90**, 155126 (2014).
 - [9] J. G. Rau, E. K.-H. Lee, and H.-Y. Kee, *Annu. Rev. Condens. Matter Phys.* **7**, 195-221 (2016).
 - [10] A. Kitaev, *Ann. Phys.* **321**, 2 (2006).
 - [11] A. Banerjee, *et. al.*, *Nat. Mat.* (2016) doi:10.1038/nmat4604.
 - [12] K. Kanoda and R. Kato, *Ann. Rev. Cond. Mat. Phys.* **2**, 167 (2011).
 - [13] B. J. Powell and R. H. McKenzie, *Rep. Prog. Phys.* **74**, 056501 (2011).
 - [14] S. M. Winter, R. T. Oakley, A. E. Kovalev, and S. Hill, *Phys. Rev. B* **85**, 094430 (2012).
 - [15] B. J. Powell, *Coord. Chem. Rev.* **295**, 46 (2015).
 - [16] R. Llusar and C. Vicent, *Coord. Chem. Rev.* **254**, 1534 (2010).
 - [17] A. L. Gushchin, R. Llusar, C. Vicent, P. A. Abramov, and C. J. Gómez-García, *Eur. J. Inorg. Chem.*, 2615 (2013).
 - [18] R. Llusar, *et. al.*, *J. Am. Chem. Soc.* **126**, 12076 (2004).
 - [19] A. C. Jacko, C. Janani, K. Koepernik, and B. J. Powell, *Phys. Rev. B* **91**, 125140 (2015).
 - [20] A. L. Khosla, A. C. Jacko, J. Merino and B. J. Powell, arXiv:1606.04605.
 - [21] J.-K. Bao, *et. al.* *Phys. Rev. X* **5**, 011013 (2015).
 - [22] H. Zhong, *et. al.*, *Phys. Rev. Lett.* **115**, 227001 (2015).
 - [23] C. Janani, J. Merino, I. P. McCulloch, and B. J. Powell, *Phys. Rev. Lett.* **113**, 267204 (2014).
 - [24] C. Janani, J. Merino, I. P. McCulloch, and B. J. Powell, *Phys. Rev. B* **90**, 035120 (2014).
 - [25] H. L. Nourse, C. Janani, I. P. McCulloch, and B. J. Powell, arXiv:1606.04297.
 - [26] P. Fazekas, *Lecture Notes on Electron Correlation and Magnetism*, World Scientific (2008), page 63.
 - [27] B. J. Powell, *Sci. Rep.* **5**, 10815 (2015).
 - [28] J. Merino, B. J. Powell, and R. H. McKenzie, *Phys. Rev. B* **73**, 235107 (2006).
 - [29] Analytic expressions for the parameters in Eqs. (3)-(4) to first order in $1/U$ and second order in H_{SO} and H_{kin} are given in the Sup. Info.
 - [30] From our calculations we estimate that residual terms are at most of $\mathcal{O}(10^{-4}t_c)$.
 - [31] A. F. Albuquerque, C. J. Hamer, and J. Oitmaa, *Phys. Rev. B* **79** 4412 (1989).
 - [32] S. Hu, B. Normand, X. Wang, and L. Yu, *Phys. Rev. B* **84**, 220402(R), (2011).
 - [33] A. Langari, F. Pollmann, and M. Siahatgar, *J. Phys. Cond. Matt.* **25**, 406002 (2013).
 - [34] Y.-C. Tzeng and M.-F. Yang, *Phys. Rev. A* **77**, 012311 (2008).
 - [35] T. Yildirim, A. B. Harris, A. Aharony, and O. Entin-Wohlman, *Phys. Rev. B* **52**, 10239 (1995).
 - [36] I. Dzyaloshinski, *J. Phys. Chem. Solids* **4**, 241 (1958).
 - [37] T. Moriya, *Phys. Rev.* **120**, 91 (1960).
 - [38] I. Affleck, T. Kennedy, E. H. Lieb, and H. Tasaki, *Phys. Rev. Lett.* **59**, 700 (1987).
 - [39] Interference effects also lead to a quasi-one-dimensional band structure in $\text{Mo}_3\text{S}_7(\text{dmit})_3$ [19] despite the similarity of t and t_z . However, these interference effects are of $\mathcal{O}(t^6)$ so they do not occur in the present $\mathcal{O}(t^2)$ analysis. They are associated with standing waves around dodecagons in the $a-b$ plane which propagate freely along the c -axis.
 - [40] K. Wierschem and P. Sengupta, *JPS Conf. Proc.* **3**, 012005 (2014).
 - [41] J.-S. Xia, *et. al.*, arXiv:1409.5971